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| (21) International Application Number: PCT/EP99/07121 (22) International Filing Date: 24 September 1999 (24.09.99) (30) Priority Data: <table border="0" style="width: 100%;"> <tr> <td style="width: 40%;">98307761.1</td> <td style="width: 40%;">24 September 1998 (24.09.98)</td> <td style="width: 20%;">EP</td> </tr> <tr> <td>9916174.7</td> <td>9 July 1999 (09.07.99)</td> <td>GB</td> </tr> <tr> <td>9916175.4</td> <td>9 July 1999 (09.07.99)</td> <td>GB</td> </tr> <tr> <td>9916176.2</td> <td>9 July 1999 (09.07.99)</td> <td>GB</td> </tr> </table> (71) Applicant (for all designated States except US): ROCKWOOL INTERNATIONAL A/S [DK/DK]; 501 Hovedgaden, DK-2640 Hedehusene (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): DYRBOEL, Susanne [DK/DK]; Freerslevvej 3, DK-4690 Haslev (DK). HANSEN, Erling, Lennart [DK/DK]; Prins Valdemars Vej 34, DK-2820 Gentofte (DK). FRICKMAN, Trine [DK/DK]; Skovvaenget 18, D-3480 Fredensborg (DK). CRIDLAND, Ian [DK/DK]; Lindemborgvej 8, DK-2720 Vanlose (DK). (74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB). | | 98307761.1 | 24 September 1998 (24.09.98) | EP | 9916174.7 | 9 July 1999 (09.07.99) | GB | 9916175.4 | 9 July 1999 (09.07.99) | GB | 9916176.2 | 9 July 1999 (09.07.99) | GB | (81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
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| (54) Title: MAN-MADE VITREOUS FIBRE PRODUCTS FOR USE IN THERMAL INSULATION, AND THEIR PRODUCTION | | | | | | | | | | | | | | |
| (57) Abstract <p>Thermal insulation products are provided which comprise air-laid MMVF material through which particulate additive is distributed substantially homogeneously, and the particulate additive is selected from the group consisting of silicon, aluminium, mica, silica and titania. The additive particles are bonded to the surfaces of the MMV fibres by a binder. The product may be a granulated product but preferably comprises a layer which is an air-laid MMVF batt or batt stratum through which the additive is distributed. Improved thermal insulation (λ value) is obtained.</p> | | | | | | | | | | | | | | |

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**MAN-MADE VITREOUS FIBRE PRODUCTS FOR USE
IN THERMAL INSULATION, AND THEIR PRODUCTION**

This invention relates to thermal insulation products based on man-made vitreous fibres (MMVF) and which are
5 modified in a simple manner so as to give improved thermal insulation as indicated by a reduced λ value.

MMVF products are known for use in various environments for thermal insulation purposes. It is desirable to try to obtain the best thermal insulation
10 properties available. Various methods for doing this have been suggested in the past.

For instance, US 3,014,872 describes one method of improving fibre glass or mineral wool. This is done by blowing into the loosely matted product a powdered
15 substance such as silicon, germanium, carbon black or fibrous potassium titanate. It is said to be essential that the powdered material is present in an amount of from 20 to 50% by weight of the fibrous material and 25 wt.% silicon is exemplified. It is stated to be important that
20 the particles have poor thermal contact with the fibres, since good thermal contact would increase thermal losses due to conduction, and that the silicon should adhere lightly to the fibres by electrostatic attraction. The product is used for insulation surrounding an oven in an
25 improved electric range.

WO92/09538 refers to US 4,101,335, which it states discloses a "fire resistant asbestos-free building board" comprising mica or a mixture of mica and standard vermiculite distributed in a calcium silicate binder.

30 US 4,919,995 describes the use of gold-coated mica flakes having thickness approximately 1 micron and area a few hundredths of a square millimeter which are distributed throughout a heat insulating device formed from quartz wool or mineral wool. It appears that the flakes must be
35 arranged in a defined pattern (juxtaposed and overlapping) and are oriented so that they are perpendicular to the

expected direction of travel of heat. Proportions of these flakes in the product are not specified.

As long ago as 1939 it was suggested in DK 56910 to use aluminium powder as a reflecting substance to improve thermal insulation of insulating materials made of glass filaments and similar filaments such as silicate, mineral and slag filaments. This material is stated to be valuable at high temperatures. Amounts and sizes are not specified although amounts of other additives are given. These are approximately 33% or approximately 0.5%.

It is well known to laminate MMVF products with sheets comprising metal such as aluminium with the intention of improving thermal insulation purposes. An example is JP-A-07/280,171.

The inclusion of metallised polymeric films, in which metallisation can be by aluminium, tin, nickel or zinc, is disclosed in JP-A-63/293,399. US 4,755,313 describes a system in which reflective fibres which are formed from metal or are coated in metal are included in a product. The coating can be aluminium. The product may also contain what is described as "insulating powder" and SiO_2 , TiO_2 and Al_2O_3 are suggested for this. Various other publications have suggested metal coated fibres for similar purposes. These include DE 4,024,488 and DE 3,925,526.

A different type of product is described in EP-B-500,900. This is produced by producing glass wool panels and subjecting them to vacuum whilst encapsulating them. A particulate material is included which must have a surface area at least $50 \text{ m}^2/\text{g}$ (by BET). Fumed and precipitated silica are exemplified and preferred, although other silicas and graphite are mentioned in the description. The very fine particles are important in the context of this type of vacuum produced product. The product must be free of binder, especially organic binder.

US 3,793,204 is also in a different area and does not concern low density, air-laid products. Instead it concerns the production of a molded composite of high

density, also for insulation purposes. This states that it is known to add titanium oxide particles to fibrous insulators of this type to attenuate radiation through absorption and scattering.

5 Various other suggestions have been made for inclusion of additives in mineral fibres so as to improve their thermal insulation properties. For instance, JP 06/034,093 describes lamination of a product with gold foil. US 4,836,837 provides layers of copper oxide on glass fibres.
10 GB 1,549,657 is similar and provides a layer of copper, cobalt, iron, chromium, manganese or nickel in metallic or oxidic form on glass fibre surfaces.

Despite all of these various suggestions, it remains desirable and commercially important to be able to provide
15 a product which has improved insulation properties and can be made in a simple and convenient manner, in particular in a manner which allows production to take place without major modification of the equipment and processes currently in use for producing the MMVF product. As far as we are
20 aware, none of the suggestions discussed, apart from those concerning lamination with various layers, have proved technically or commercially useful.

According to the invention we provide a thermal insulation product comprising air-laid MMVF material
25 throughout which a particulate additive is distributed substantially homogeneously, characterised in that the additive is selected from the group consisting of silicon, aluminium, mica, silica, titania and mixtures thereof and the particulate additive is held in the MMVF material by
30 being bonded to the surfaces of the MMV fibres by a binder.

We find that the selection of this particular group of materials is surprisingly beneficial in reducing λ value. In particular, we find that the construction of the invention allows excellent reduction in λ value at very low
35 levels of particulate additive, in particular lower levels than those described in the prior art.

Of the selected materials, we find that silicon, aluminium and mica, especially silicon and aluminium, and in particular aluminium, are especially beneficial. When aluminium is used it can be used as powder or flakes, preferably flakes.

In the invention it is essential that the particulate additive is bonded into the MMVF product with a binder. This is contrary to suggestions in the prior art in, for instance, US 3,014,872 which teaches that limited contact is important.

The MMVF product may be a bonded product, in which case part or all of the binder for the product can conveniently also serve as binder for the additive.

Alternatively, a separate binder for the additive may be provided.

The product may be a granulate, but a preferred thermal insulation product according to the invention comprises a layer which is an air-laid MMVF batt or batt stratum through which the particulate additive is distributed substantially homogeneously.

The product may comprise only MMVF which contains the additive or may have MMVF regions without it (eg in the case of a batt having an additive-containing layer). Preferably the MMVF part of the product consists essentially of MMVF having homogeneously distributed additive.

This product may comprise a batt having the additive distributed substantially homogeneously throughout most or all of the batt, in which event the defined layer substantially has the thickness of the batt. However the products of the invention include those in which the layer is a stratum of the batt, that is to say that it is a layer within a batt. For instance the batt stratum, that is to say the layer which contains the particulate additive, may be from 10 to 80%, often 10 to 20% or 50%, of the thickness of the entire batt. Batts of the invention may comprise more than one layer in which the particulate additive is

homogeneously distributed. The layers are disposed perpendicular to the expected direction of heat transfer.

The particulate additive can be distributed uniformly throughout the layer or there may be a concentration gradient. Irrespective of whether or not there is a concentration gradient, the additive is distributed substantially homogeneously in the sense that it should be sufficiently uniformly distributed throughout the volume of the product to minimise the risk of significant amounts of radiation being able to pass through the level without encountering the additive. Accordingly the areas of the layer which are substantially free of additive should be as low as possible.

It is possible, with the invention, to obtain a significant improvement (reduction) in λ by including the additive. For instance it is easy, by the invention, to reduce the λ value of a batt by at least 0.5 units (e.g. from 35.5 mW/mK down to 35.0) and generally by at least 0.8 or 1 unit (e.g. 1 to 3 units or more).

In general it is well-known that air-laid MMVF insulation products generally show a decrease in λ as density increases (to an eventual minimum at very high density). Thus in the invention it is possible to provide a product of equivalent density but lower λ and hence better thermal insulation, or a product with equivalent λ and thermal insulation properties at lower density. Further, a lower thickness can be used to give equivalent insulation value. Thus it is possible to improve insulation properties in a given situation, which is of course beneficial, and it is also possible to obtain equivalent insulation behaviour with a lower density product or with a lower thickness of insulation. The latter system is of particular value for use in aeroplanes and other vehicles because of the ability to reduce weight and thus reduce fuel requirements for the vehicle.

The ability to provide lower density also gives transportation and storage advantages. Lower density

products have greater compressibility. However, they also retain good recovery. Therefore a lower density product can be compressed to reduce its volume for transportation and then recover substantially all its original thickness for use (in particular to the thickness of an equivalent product without additives). The invention allows the achievement of lower density (and hence higher compressibility) at equivalent or even better λ value. For instance, a product according to the invention and containing aluminium can be provided at a density of 29 kg/m³ with λ_{10} of 35 mW/mK, in contrast to a product not containing any aluminium which has density of 34 kg/m³ but the same λ value. The compressibility of the 34 kg/m³ product is 22% whereas the compressibility of the 29 kg/m³ product is 30%. Thus the 29 kg/m³ product may be transported more efficiently and does not have impaired recovery.

Thus preferred products of the invention, especially products which are a batt, are products which have been compressed by at least 25%, preferably at least 30%. The density before compression is preferably not more than 30 kg/m³. The product is preferably releasably compressed, ie when the compression force is removed it recovers substantially all of its pre-compression thickness (for instance at least 70% of its pre-compression thickness). Such compressed products are often usefully produced for transportation and storage purposes. The invention also includes the production of a product of the invention, especially a batt product, having density of not more than 30 kg/m³ and compression of that product by at least 25%, preferably at least 30%. The λ_{10} of the pre-compressed product is preferably not more than 45 mW/mK, more preferably not more than 40 mW/mK, or even more preferably not more than 37 mW/mK.

The amount of particulate additive in the product or layer is usually at least 0.2% by weight of the product in order to give a useful increase in performance, and is

generally at least about 0.4 or 0.5% by weight. Preferably it is at least 1% by weight. The amount is generally not more than 15%, preferably not more than 10%. It can be not more than 6%. For rock, stone or slag wool fibres in particular the amount is preferably lower. In this case the amount is preferably not more than 10%, more preferably not more than 7% or 6%. It is particularly surprising in view of the disclosures in prior art references of the necessity for amounts of 20% or greater that with the selection of products into which the particulate additive is bonded we can achieve excellent results with such low amounts. Preferred amounts are from 0.5 to 10%, preferably 1 to 6% by weight of the product.

The MMV fibres can be any man-made vitreous fibres which are suitable for the production of low density thermal insulation. Accordingly the fibres can be glass, rock, stone or slag fibres. The fibres can have any suitable dimensions, for instance those which are conventional in the production of low density and thermal insulation products. Generally the average fibre diameter is below 10 μm , eg below 5 μm , and can be the same as conventional fibre diameter or less.

According to the invention particularly beneficial results can be achieved by selecting the particle size range for the particulate additive.

Particle size can be measured by a laser scattering technique. Suitable equipment for such techniques include those available from, e.g., Malvern Instruments and Sympatec Helos. The laser scattering technique provides various size and size distribution properties. In the invention the average particle size is the volume median diameter, often described as d_{50} . This is the median value in the volume distribution calculated by the laser scattering method. This value is commonly used by suppliers of particulate materials to denote average particle size.

Preferably this average particle size is not more than 100 μm , more preferably not more than 20 μm and in particular not more than 10 μm , especially not more than 5 μm . Particularly good results can be achieved with
5 particles of average size not more than 4 μm , and in particular not more than 3 μm .

The average particle size is usually at least 0.01 μm and generally at least 0.1 or 0.5 μm . Best results are generally obtained when the average particle size is
10 between about 0.5 and 10 μm , preferably about 1 to 3 or 4 μm .

It is also preferred that the d_{90} value (ie 90% of the particles in the volume distribution are below this value) is not more than 20 μm , in particular not more than 10 μm ,
15 preferably not more than 8 μm . Particularly good results can be achieved when d_{90} is not more than 6 μm .

Preferably d_{10} (ie 10% of particles in the volume distribution are below this value) is at least 0.1 μm , more preferably at least 0.5 μm , in particular at least 0.8 or
20 1 μm .

Good results can also be achieved by selecting appropriate surface area values, in particular in combination with the preferred particle size ranges above. Surface area can be calculated from the laser scattering
25 measurements obtained by the above methods. In this case, surface area is generally above 0.1 m^2/g , preferably above 0.5 m^2/g . Preferably it is at least 0.8 m^2/g . It may range up to 10 m^2/g or higher.

An alternative and preferred method for measuring
30 surface area is the well known BET method. This provides a specific surface area value. When measured by this method the surface area is generally above 0.5 m^2/g , preferably above 1 m^2/g . More preferably it is at least 5 m^2/g , most preferably at least 10 m^2/g . It may range up to
35 20 m^2/g or higher, and is preferably not more than 30 m^2/g , more preferably not more than 20 m^2/g .

When the particulate additive comprises aluminium, or mica, these may be in the form of powder or, preferably, flakes. These generally have surface area of from 2 to 10 m²/g (BET). The other additives are preferably in the form of powder. The additives, especially silicon, may be coated, for instance with acrylic polymer.

The batt or granulate generally consists substantially only of MMV fibres, the particulate additives, binder and minor additives such as oil. It is usually free of combustible or organic fibres.

The granulate or batt, and (in a batt product) the or each layer which consists of part or all of the thickness of the batt, must be low density, and in practice usually has a density of below 300 kg/m³ and preferably below 150, and most preferably below 120 kg/m³. Density is usually at least 5, preferably at least 7 kg/m³. Preferably it is from 10 to 150 kg/m³.

We find that particularly good improvements in λ value can be obtained when the density is 60 kg/m³ or less, for instance not more than 40 kg/m³, in particular not more than 30 kg/m³. Suitable applications for materials having density in this range are general building insulation. The invention can thus be beneficial in applications in which the product is required to have very low density, such as flight insulation (eg from 10 to 20 kg/m³). The density may be below 10 kg/m³, for instance from 5 to 8 kg/m³.

The invention also gives benefits in products having density greater than about 40 kg/m³ and these include building insulation products where high strength is required, lamellar products and technical insulation.

An advantage of the invention is that it may be applied at a wide range of temperatures. The products may be used for high temperature insulation above 300°C, for instance up to 500 or 800°C. However the products are also useful for improving insulation properties at low temperatures, for instance down to -80°C, for instance down to -20°C. It is particularly beneficial and surprising

that the additives give improved insulation across this entire range.

One preferred range for use in the invention is from -80°C to 30°C. Products of the invention can be used at such temperatures in applications such as flight insulation and cold storage.

The invention is also useful for applications such as building insulation, and technical insulation (e.g. insulation of pipes for hot water or ventilation) at temperatures of from -30 to 100°C.

A further range of high temperatures at which the invention is useful is from 80 to 300°C. Suitable applications include technical insulation (.e.g. for boilers and steam pipes).

The invention may especially be used to give effective insulation at temperatures above 300°C, for instance up to 500°C and even up to 800°C.

Suitable amounts of binder are 0.1 to 20 or 10%, generally 0.5 to 7%, preferably 1 to 5%, by weight binder solids based on the dry weight of the product. The binder is applied as an aqueous solution and the additive can be included as a suspension in this solution.

The binder for the additive can be inorganic such as sodium or potassium or lithium silicate, silicophosphate, monoaluminium phosphate or silica sol.

Often the binder for the additive is organic and can be any of the conventional curable binders which are known for MMVF batts. Suitable binders include curable and non-curable binders and examples are those based on phenol, urea, resorcinol, furanic binders or melamine, and in particular resins formed by reacting the above with formaldehyde. Curable and non-curable acrylic binders, polyvinyl acetate, polyamides, polyimides, polyamides/-imides, polyesters, modified starches, chitosan, dopa, tannin, xanthan and other gums, cellulose derivatives, alginates, thermoplastics and mixtures thereof may be used. The amount of organic binder is usually not more than 20%,

preferably not more than 10%, and generally not more than 7%, with preferred amounts being below 5%. These percentages are by weight binder solids based on the dry weight of the product. Inorganic and organic binders may also be used in combination. The additive can be included as a suspension in the aqueous binder.

The dry weight of total binder in the final batt is preferably below 10%, usually below 7%, and more preferably below 4 or 5% by weight.

We find that the amounts of binder which are used are slightly greater than those which would be required for equivalent products without the selected additive. In particular, we find that additional binder in an amount of around 0.1 to 1, preferably 0.1 to 0.5, more preferably 0.2 to 0.3 (eg about 0.25) parts binder per part additive is required in addition to the standard amount which would be used in the absence of additive. Total amounts of binder are often at least 0.5 or 1% by weight of the total product.

In the invention we find it is not necessary (as for instance in US 4,919,995 above) to orient the particles of additive or prearrange them within the product. In the invention they may be and preferably are randomly oriented within the product and, if the product is a batt, within the or each layer or the batt.

The thermal insulation product may consist solely of the batt or granulate. Thus it can consist of either the batt containing the particulate additive distributed throughout its thickness or a batt stratum which contains particulate additive and which is integral with the remainder of a batt which is otherwise free of particulate additive. However if desired a batt product can comprise other materials, for instance one or more other air-laid MMVF batts and/or decorative or structural materials such as foil.

The term "batt" includes very flexible roll products such as those used for insulation for pipes or boiler

insulation, as well as less flexible (or even inflexible) products, for instance those in the form of slabs.

The batt product can be shaped in conventional shapes, for instance pipe sections for use as insulation for pipes or for boiler installations or for general building insulation. Accordingly, the product can have shapes such as cylindrical, part cylindrical or substantially rectangular slabs and rolls.

The invention is also useful when the product is not in the form of a batt but is in the form of granulated material such as is used for general building insulation. These materials are generally formed by granulating pre-formed batts and are thus produced by a process comprising formation of a batt.

Although the products of the invention are particularly beneficial in thermal insulation applications, they may also be used in other applications for which MMVF products are known, for instance fire protection and prevention and acoustic insulation.

The batt can be made in conventional manner, for instance by forming a cloud of man-made vitreous fibres entrained in air by fiberising mineral melt into an air stream and air-laying the fibres on to a collector as a web, and converting the web to a batt in conventional manner. This conversion can involve, for instance, cross-lamination of the web and drying, melting or curing of any binder that is present.

In the invention, particulate additive can be distributed through some or all of the thickness of the eventual batt by including it in part or all of the cloud of fibres as they are formed and collected. Depending on how the particulate additive is distributed within the cloud, it will then be distributed uniformly throughout the web or will be distributed through part only of the web. It is then possible, in conventional manner, to form a batt which either has particulate additive distributed throughout its thickness or through part only of its

thickness. Suitable systems include those described in our International Patent Application number PCT/EP99/02149.

The additive can be included in the cloud of fibres either by injecting it into the cloud, either from around
5 or from within the cloud, or by injecting the additive into the cloud during the formation of the fibres.

For instance the mineral melt is generally fiberised using either a centrifugal fiberising apparatus such as a disk or cup which rotates about a substantially vertical
10 axis or a cylinder or disk which rotates about a substantially horizontal axis. In the latter case it is usually a cascade of cylinders which is used. This initially forms an annular cloud of fibres, and the additive can be injected into this annular cloud from the
15 centrifugal fiberising apparatus.

Preferred apparatus and methods are described in our International Patent Publications WO97/20779 and WO97/20781. These apparatus and methods are particularly useful when the additive has particle size from 5 microns
20 and up.

Finer particles may be distributed using a conventional centrifugal distribution means which is attached to and rotates coaxially with one or more of the cylinders, or via spray nozzles placed inside or outside
25 the annular cloud (such as are used as conventional binder supply nozzles).

This process of the invention is especially beneficial because the particulate additive is added in simple and convenient manner. There is no need to devise additional
30 processing steps, for instance for arranging the particles in the product (as is necessary in US 4,919,995). Furthermore, uniform and homogeneous distribution of the additive is promoted by its inclusion during formation of the fibres, rather than after collection (as in US
35 3,014,872).

The additive may be added as a powder or as a slurry in water or as a slurry in aqueous binder. The aqueous

binder may be the binder for the batt or a separate aqueous binder solution. Part of the additive may be added with the binder for the batt and part added with a separate binder solution. We find surprisingly that including the additive in this simple manner by means of apparatus which is conventionally available for inclusion in MMVF production equipment gives excellent results without the need to orient or place the particles within the product.

We find benefits when the additive is added as a slurry in a liquid in which is included a dispersing agent. Preferably the amount of dispersing agent in the slurry is 0.1 to 2%, preferably 0.1 to 1.0%, dry weight dispersing agent based on weight of slurry.

The slurry can also include defoamer (antifoaming agent) in an amount of from 0.01 to 2 wt %, preferably 0.1 to 1.0 wt %, by weight of slurry, and/or 0.05 to 1 wt %, preferably 0.1 to 0.5 wt %, by weight of slurry, of anti-settling agent.

When the slurry is added separately from the binder for the product, the amount of additive in the slurry is from 10 to 60%, preferably 20 to 50% by weight additive based on weight of slurry. When the additive is added with the binder for the product a slurry of this concentration is generally first produced and then mixed with the binder for the product. In that case, the eventual amount of additive in the slurry applied to the fibres may be as low as 0.5% but is often at least 0.8% and preferably at least 2%.

Another (less preferred) way of making the products of the invention is by collecting the web of fibres (without prior addition of additive) and then impregnating the additive into the web, for instance on the collector, and then converting the web to a batt.

Another way of making the products is by forming a batt in conventional manner, for instance as described above, and then impregnating part or all of the thickness of the batt with the additive. This method is less

preferred, as uniform distribution can be difficult to obtain, except for thin layers.

In these techniques also the additive may be added as powder or as a slurry in water or as a slurry in aqueous binder (either the binder for the batt or a separate aqueous binder solution). It is essential that the additive is bonded to the surfaces of the fibres.

We find that the proportion of additive in the final product (wt.% based on weight product) is usually slightly lower than the proportion included in the process (wt.% based on fibres forming). Thus usually the proportion included in the process is approximately 1.3 times the final proportion required in the product, ie about 75% of the amount added appears in the product.

The additives may be included by the process described in our co-pending Application No. PCT/EP99/... (reference PRL04286GB), the disclosure of which is incorporated herewith by reference. In this process the additive is included using apparatus comprising

a set of at least three rotors mounted on a housing each for rotation about a different substantially horizontal axis and arranged such that when the rotors are rotating melt poured onto the periphery of the top rotor in the set is thrown onto the periphery of each subsequent rotor in turn and fibres are thrown off the rotors,

air supply means for blowing the fibres axially along the chamber and which comprise a primary air supply slot associated with each subsequent rotor wherein each slot has an internal diameter substantially the same as the external diameter of the periphery of its associated rotor and is constructed for discharging a primary air blast substantially parallel to that periphery as a wall jet, and

additive supply means on or adjacent the spinner, preferably at least one additive discharge orifice on each (or any) of the subsequent rotors positioned within the periphery of the rotor and rotating with the rotor, for spraying additive outwardly onto the fibres as they are

thrown off the rotor and are carried forward from the rotor,

and in which process fibres are formed by pouring melt onto the top rotor while the rotors are rotating, the air
5 blasts are being discharged and the additive is being sprayed outwardly, and thereby forming a cloud of fibres and additive travelling forwards from the spinner, and collecting the fibres and additive from the cloud as a web, and if necessary converting the web to the insulation
10 product,

and in which each air blast emerges from the air supply orifice with a velocity of at least 100m/sec.

The additive and the product may have any of the preferred features discussed above.

15 We find that this process provides even greater improvements in λ value.

Typical products of the invention made from rock, stone or slag wool by centrifugal fiberising apparatus (such as a cascade spinner) comprise 60 to 75 wt% fine
20 mineral fibre, 2 to 4 wt% binder and 23 to 36 wt% shots (for instance having an average size above 63 μ m).

The products of the invention may also contain (bonded to the MMVF product) graphite particles in addition to the additives defined above. Inclusion of graphite is
25 described in our co-pending Application No. PCT/EP99/... (reference PRL04151GB) and its disclosure is incorporate herein. Preferred ratios of graphite: other additives are 1:99 to 50:50, more preferably 5:95 to 40:60.

The following are examples.

30 Example 1

73 kg of a 20% aqueous, phenolic curable binder is mixed with 77 l tap water followed by 1.4 kg dispersing agent which is a sodium salt of maleic acid-olefin copolymer (available from BASF under the tradename
35 Pigmentverteiler MD 20) and 0.4 kg defoamer which is an aromatic mineral oil with added silica and acrylic polymer (available from Henkel-Nopco under the tradename NOPCO

8034-M). The liquid is slowly mixed for 5 min. 51 kg particulate additive is slowly added while stirring. The rate of stirring is increased and the batch is dispersed for 15 min. This dispersion is stable for several days.

5 A mineral melt is fiberised using a cascade spinner of conventional type having at least three substantially cylindrical rotors mounted for rotation about a horizontal axis, whereby melt poured onto the top rotor is thrown from one rotor to the next in series and is fiberised. An
10 airstream flows from the rotors in conventional manner to carry the fibres as a cloud towards a permeable inclined collector, where the fibres are collected as a web in conventional manner.

The aqueous binder and additive slurry is injected
15 into the cloud as it is formed using the conventional binder supply tubes on the fibre forming apparatus.

The web is then cross-lapped to form an uncured batt. This is then passed through an oven to cause curing.

Example 2

20 Various tests are carried out using different particulate additives, added using a process essentially as in Example 1. In the reference test no additive was included. In Test 1, 6 wt.% (added based on amount of wool produced) SiO_2 (average size $0.15\mu\text{m}$, surface area $20\text{ m}^2/\text{g}$
25 by BET) is added to the product. In Test 2, 4 wt.% (added based on total wool produced) TiO_2 (average size $3\mu\text{m}$) is added. In Test 3, 4.5 wt.% (added based on total wool produced) silicon (average size $3.5\mu\text{m}$, surface area $1.1\text{ m}^2/\text{g}$ by laser scattering) is added. In Test 4, 4 wt.%
30 (based on total wool produced) mica (average size $5\mu\text{m}$, surface area $8.4\text{ m}^2/\text{g}$ by laser scattering) is added. In Test 5, 4 wt.% (based on total wool produced) aluminium powder (average size $6\mu\text{m}$, surface area $1.2\text{ m}^2/\text{g}$ by laser scattering) is added. In each case, the proportion of
35 additive in the final product is lower by a factor of about 0.75. The thermal conductivity of each of the products

was measured at 10°C in accordance with the ISO 8301 norm. Results are shown in Table 1.

Table 1

| Sample | ρ [kg/m ³] | λ measured [mW/mK] | $\Delta\lambda$ |
|---------------------------|--------------------------------|----------------------------------|-----------------|
| Ref 1 | 28.7 | 36.2 | - |
| Test 1 (silica) | 28.4 | 35.8 | 0.4 |
| Test 2 (titanium dioxide) | 30.3 | 35.9 | 0.3 |
| Test 3 (silicon) | 25.5 | 34.7 | 1.5 |
| Test 4 (mica) | 26.5 | 35.4 | 0.8 |
| Test 5 (aluminium powder) | 29.1 | 34.9 | 1.3 |

Other suitable combinations of additives are as follows:

- (a) 6 wt.% SiO₂, average size 0.15 μm , surface area 20 m²/g by laser scattering.
- (b) 6 wt.% TiO₂, average size 5 μm .
- (c) 4.5 wt.% silicon, average size 3.5 μm , surface area 6.2 m²/g by laser scattering.
- (d) 4 wt.% mica, average size 2 μm , surface area 8.4 m²/g by laser scattering.

Example 3

141 kg of a 20% aqueous, phenolic, curable binder mixed with 152 l tap water followed by 3.3 kg dispersing agent and 4.0 kg defoamer. The liquid is slowly mixed for 5 min. 94 kg silicon having a mean particle size of 3.5 μm is slowly added while stirring. The rate of stirring is increased and the batch is dispersed for 15 min.

The aqueous binder and silicon slurry is injected into the cloud of fibres as it is formed using the conventional binder supply tubes on the fibre forming apparatus.

Example 4

Further tests are carried out using graphite and other additives, added substantially as in Example 1. Results are in Table 2 below.

Table 2

| Sample | Additive | Density (kg/m ³) | λ measured (mW/mK) | $\Delta\lambda$ (mW/mK) |
|--------|-------------------------------------|---------------------------------|-------------------------------|----------------------------|
| Ref 2 | - | 29.5 | 35.4 | - |
| Test 3 | 3 wt.% graphite 4 wt.% silica | 29.4 | 33.8 | 1.6 |
| Test 4 | 4.5 wt.% graphite 6 wt.% silicon | 27.3 | 32.8 | 2.6 |

CLAIMS

1. A thermal insulation product comprising air-laid MMVF material through which particulate additive is distributed substantially homogeneously, characterised in that the
5 particulate additive is selected from the group consisting of silicon, aluminium, mica, silica and titania and mixtures thereof and the particles of additive are held in the product by being bonded to the surfaces of the MMV fibres by a binder.
- 10 2. A thermal insulation product according to claim 1 which comprises a layer which is an air-laid MMVF batt or batt stratum and the particulate additive is distributed substantially homogeneously throughout the layer.
- 15 3. A product according to claim 1 or claim 2 in which the particulate additive has a volume median particle size d_{50} measured by a laser scattering technique of not more than $12\mu\text{m}$, preferably not more than $5\mu\text{m}$, more preferably not more than $3\mu\text{m}$.
- 20 4. A product according to claim 1 or claim 2 in which the particulate additive has a volume median particle size d_{50} measured by a laser scattering technique of at least $0.5\mu\text{m}$, preferably at least $1\mu\text{m}$.
- 25 5. A product according to any preceding claim in which the particulate additive has a surface area measured by a laser scattering technique of at least $0.5\text{ m}^2/\text{g}$, preferably at least $0.8\text{ m}^2/\text{g}$, more preferably at least $1\text{ m}^2/\text{g}$.
- 30 6. A product according to any preceding claim in which the particulate additive has specific surface area measured by BET of at least $0.5\text{ m}^2/\text{g}$, preferably at least $5\text{ m}^2/\text{g}$, more preferably at least $15\text{ m}^2/\text{g}$.
7. A product according to any preceding claim in which the particulate additive has specific surface area measured by BET of not more than $30\text{ m}^2/\text{g}$, preferably not more than $20\text{ m}^2/\text{g}$.
- 35 8. A product according to any preceding claim in which the MMVF material is bonded by a binder, preferably organic

binder, and the particulate additive is held in the product by this binder.

9. A product according to claim 8 containing binder in an amount of from 0.1 to 20% of the MMVF material.

5 10. A product according to any preceding claim in which the amount of additive is at least 0.2%, preferably at least 0.5%, and more preferably at least 1% by weight based on weight of the MMVF material through which it is distributed homogeneously.

10 11. A product according to any preceding claim in which the amount of additive is not more than 15%, preferably not more than 10% by weight based on weight of the MMVF material through which it is distributed homogeneously.

12. A product according to any preceding claim which has
15 a density of from 5 to 300 kg/m³, preferably not more than 150 kg/m³, more preferably not more than 60 kg/m³, most preferably not more than 40 kg/m³.

13. A product according to claim 2 which has been releasably compressed by at least 25%, preferably at least 30%.

20 14. A product according to claim 1 which is a granulated MMVF product.

15. Use of a product according to claim 1 as a thermal insulation product, preferably at a temperature of from -80 to 800°C.

25 16. Use according to claim 15 at a temperature of from -80 to 30°C.

17. Use according to claim 15 at a temperature of from -30 to 100°C.

30 18. Use according to claim 15 at a temperature of from -20 to 300°C.

19. Use according to claim 15 at a temperature of from 80 to 800°C.

20. A process of making a product according to claim 1 or claim 2 comprising forming a cloud of man-made vitreous
35 fibres entrained in air by fiberising mineral melt into an air stream, including the particulate additive in part or all of the cloud of fibres, air-laying the fibres and

additive on a collector as a web, and converting the web to a batt.

21. A process according to claim 20 in which the particulate additive is included in an amount of at least 0.2%, preferably at least 0.5%, more preferably at least 1%, by weight based on weight of fibres produced.

22. A process according to claim 20 in which the particulate additive is included in an amount of not more than 15%, preferably not more than 10%, more preferably not more than 7%, by weight based on weight fibres produced.

23. A process according to claim 20 in which the particulate additive is included in the cloud as a dispersion of additive in aqueous binder for the batt.

24. A process according to claim 20 in which the particulate additive is included in the cloud as a dispersion of additive in aqueous binder separate from the binder for the batt or as a slurry in water.

25. A process according to claim 20 in which the additive is included in the cloud as a dispersion of additive in aqueous binder or in water, in which the dispersion also contains a dispersing agent, preferably in an amount of from 0.1 to 2% by weight of the dispersion.

26. A process according to claim 20 in which the additive is included in the cloud as a dispersion of additive in aqueous binder or in water, in which the dispersion also contains a defoamer, preferably in an amount of from 0.01 to 2% by weight of the dispersion.

27. A process according to claim 20 in which the additive is included in the cloud as a dispersion of additive in aqueous binder or in water, in which the dispersion also contains an anti-settling agent, preferably in an amount of from 0.05 to 2% by weight of the dispersion.

28. A process according to claim 20 additionally comprising compressing the batt product by at least 25%, preferably at least 30%.

29. A product according to any of claims 1 to 14, a use according to any of claims 15 to 19 or a process according

to any of claims 20 to 28 in which the additive is selected from the group consisting of silicon, aluminium and mica.

30. A product, use or process according to claim 29 in which the additive is silicon or aluminium.

5 31. A product, use or process according to claim 29 in which the additive comprises aluminium in the form of flakes.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/07121

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C25/02 C04B30/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C C04B C03B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X | GB 2 319 770 A (ROCKWOOL INT) 3 June 1998 (1998-06-03) page 7, line 1 - line 24 | 1-31 |
| X | DE 195 46 979 A (GRUENZWEIG & HARTMANN) 3 July 1997 (1997-07-03) the whole document | 1-29 |
| A | US 4 101 335 A (BARRABLE VICTOR ERNEST) 18 July 1978 (1978-07-18) cited in the application | 1-31 |
| | -/- | |

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/07121

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | <p>US 3 312 569 A (T.E. PHILLIPS) 4 April 1967 (1967-04-04) column 2, line 34 - line 44</p> | 1-31 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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